Overview

- H_2 production technologies and comparative assessments
- Conversion of natural gas
- Catalytic conversion of CH_4
- Reforming Technologies for producing H_2
- Simulation with ASPEN Plus
- Process flowsheet and results summary
- Findings and remarks

Assessments of H_2 Production Processes

Process	Efficiency (%) Energy	Exergy
Steam Methane Reforming (H/C based)	86	78
Coal gasification (H/C based)	59	49
Current –Technology water electrolysis (Non H/C based)	30	26
Advanced –Technology water electrolysis (Non H/C based)	49	41
Thermo-chemical water decomposition (Non H/C based)	21	19
SMR/current-tech. water electrolysis (integrated)	55	48
SMR/advanced-tech. water electrolysis (integrated)	70	62
SMR/thermo-chemical water electrolysis (integrated)	45	40

M. A. Rosen and D.S. Scott, Intl. J. of Hydrogen v23, n8, pp 653-659

Conversion of Natural Gas

- Conversion of natural gas to generate H_2 has been a challenging issue. The processes may me classified in to two groups: direct and indirect process.
- The general stoichiometric reaction is

$$C_nH_m = n\,C + m/2\,H_2$$

- Reaction temperature: 2200-2300 K
- Conducted at atmospheric pressure
- Conversion rate is 70%

Non-catalytic Conversion of CH_4

- Thermal or non-catalytic decomposition of methane requires elevated temperatures (1200-1500^{o}C).
- Special catalysts is required for decomposing methane at relatively low temperatures.
- Prospective catalysts include supported transition metal-based catalysts and metal oxides.
- This effort is based on a three-step approach:
  - reaction engineering,
  - reactor engineering and
  - process engineering.

Thermo-catalytic Conversion of CH_4

- The thermocatalytic decomposition of methane was studied over various catalysts and supports in a wide range of temperatures (500-1000^{o}C)

- Ni- and Fe-containing catalysts demonstrated relatively high efficiency and stability (for several hours) in the methane cracking reaction at moderate temperatures (600-800 ^{o}C)

Catalytic Cracking of Methane

- Direct catalytic cracking of CH_4 into H_2(gas) and C(solid) followed by catalyst regeneration in oxidative atmosphere is an attractive alternative

$$CH_4 \rightarrow C + 2H_2 \qquad \Delta H_{298} = 75 \text{ kJ/mol} \qquad (1)$$

$$C + 1/2\, O_2 \rightarrow CO \qquad \Delta H_{298} = -111 \text{ kJ/mol} \qquad (2)$$

$$C + O_2 \rightarrow CO_2 \qquad \Delta H_{298} = -283 \text{ kJ/mol} \qquad (3)$$

- CO_2 can be separated in time for H_2 production, since in CO_2 are formed during the coke removal from the catalytic surface
- Nickel is known as one of the active catalyst in CH_4 cracking at low temperature (around 500°C)
- Conversion rate of CH_4 to H_2 is 40%-50%

Steam Methane Reforming (SMR)

- Indirect processes which include conversion of CH_4
- Most important and popular chemical process for H_2 generation
- Involves five species in two reversible reactions.

$$CH_4 + H_2O = CO + 3H_2 \qquad \Delta H_{298} = 206 \text{ kJ/ mol} \qquad (1)$$

$$CO + H_2O = CO_2 + H_2 \qquad \Delta H_{298} = -41 \text{ kJ /mol} \qquad (2)$$

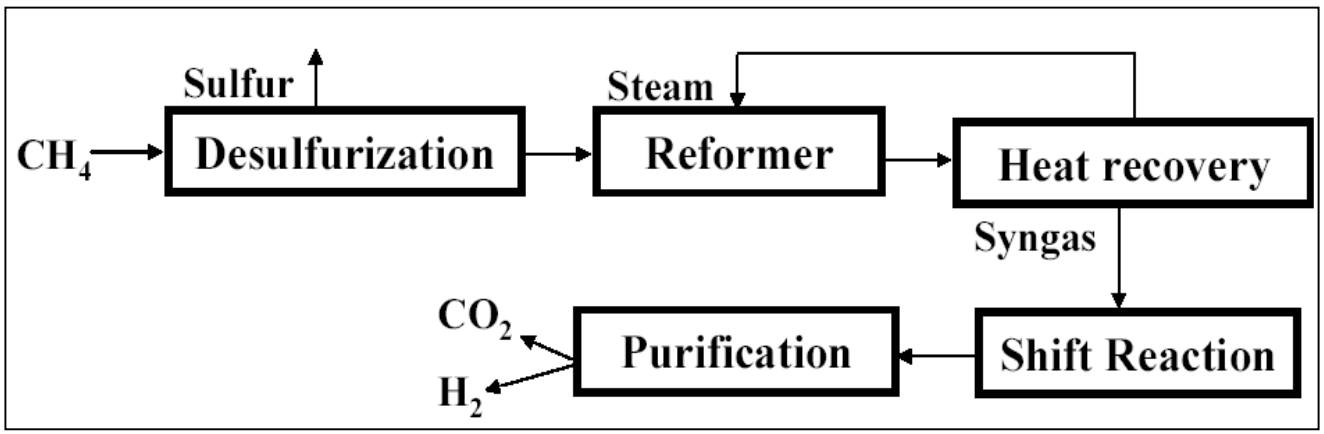
- Overall reaction :

$$CH_4 + 2H_2O = CO_2 + 4H_2 \qquad \Delta H_{298} = 165 \text{ kJ /mol} \qquad (3)$$

A. Heinzel, B. Vogel, P. Hubner, J. of Power Sources, 105(2002) 202-207

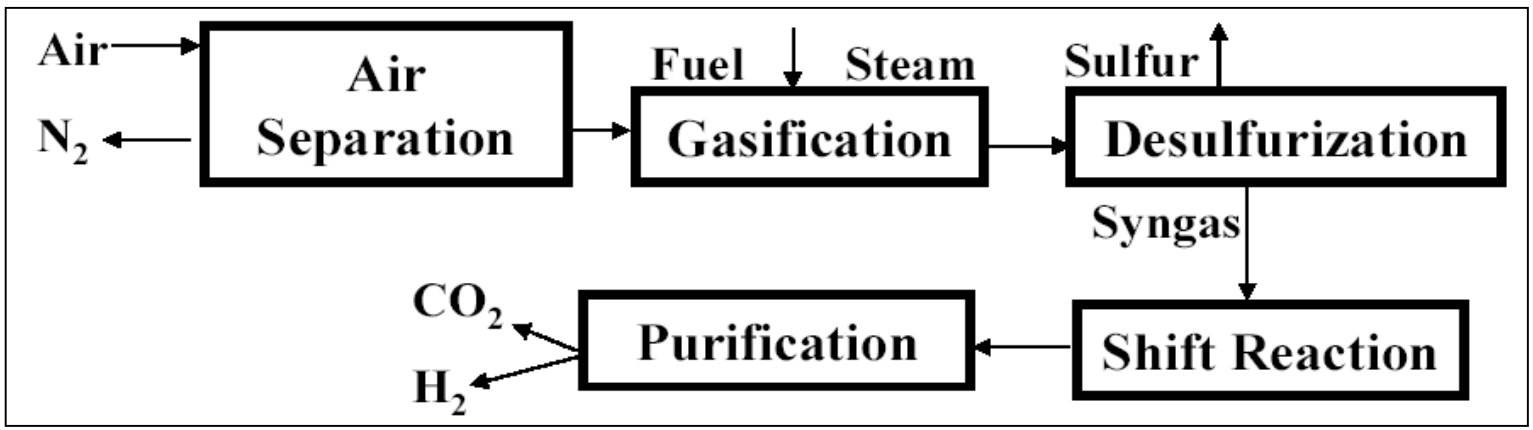
Steam Methane Reforming (SMR) – 4 Main Steps

- pretreatment process
- a reformer reactor
- a shift reactor
- gas purification process



Partial Oxidation (POX) – 4 Main Steps

- pretreatment process
- a reformer reactor
- a shift reactor
- a gas purification process



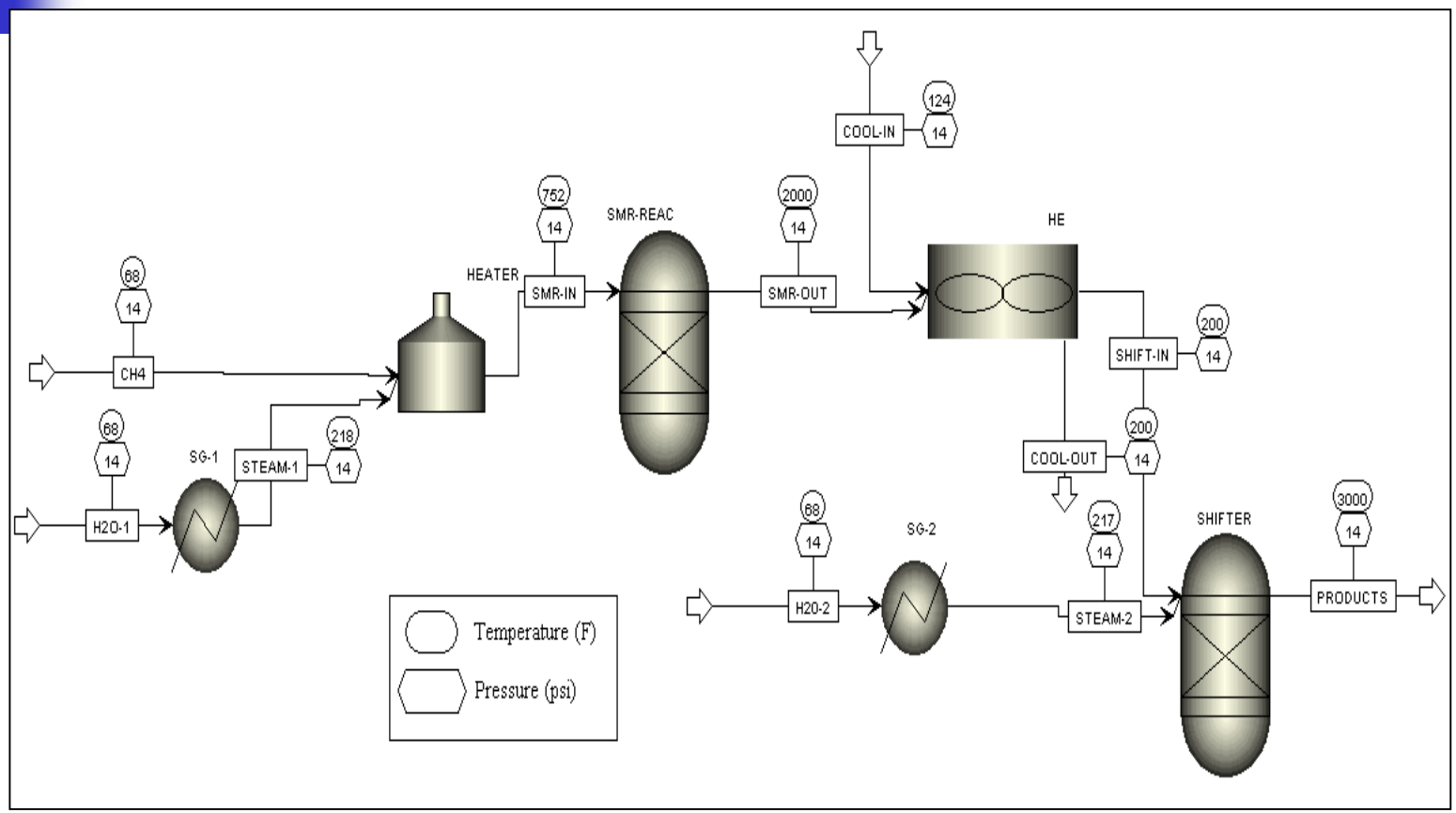
Autothermal Reforming (ATR) Process

- ATR integrates POX with SMR
- ATR have low energy requirement and high gas velocity
- The general reaction mechanism for ATR reactor:

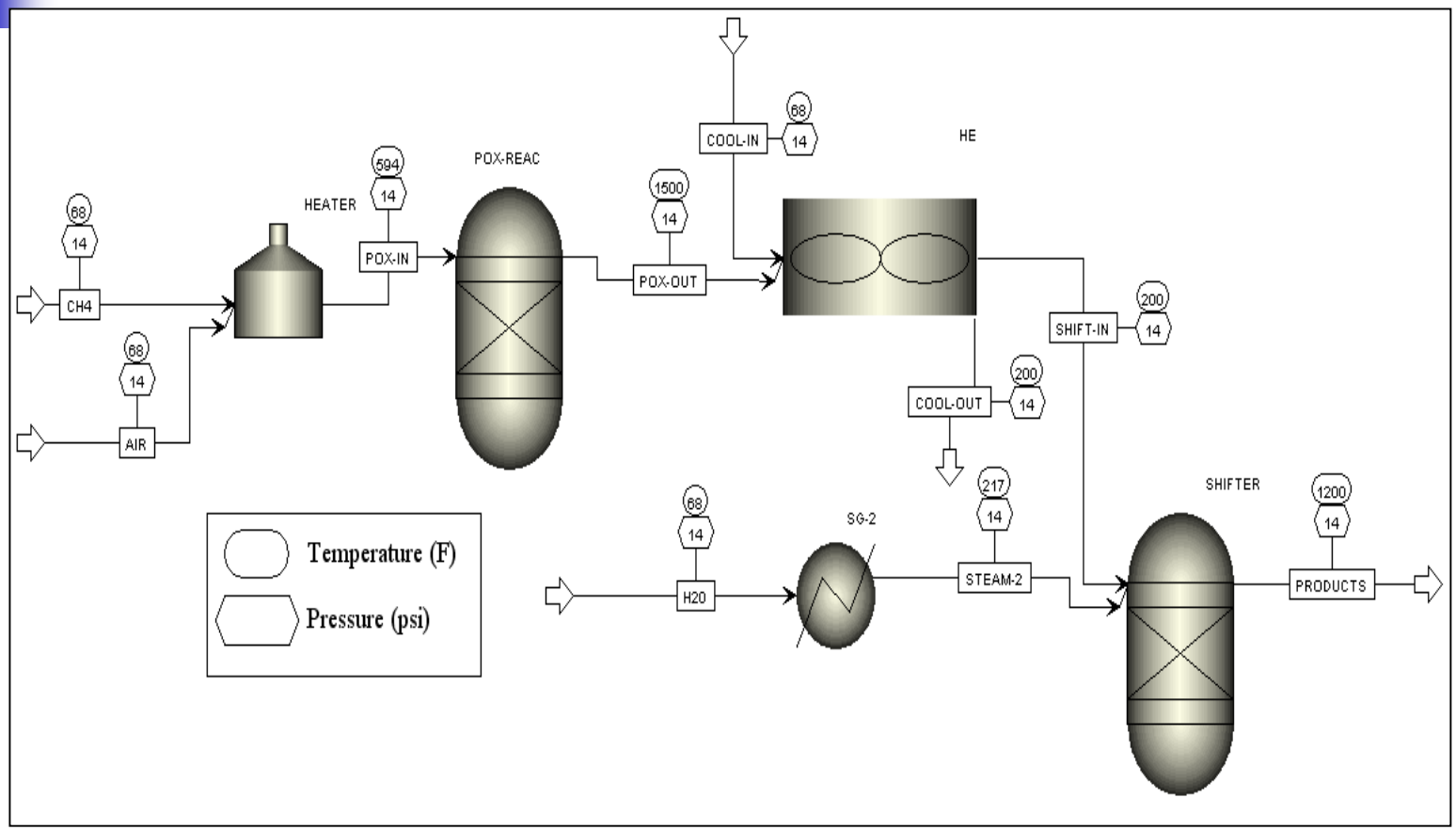
  $CH_4 + \alpha O_2 + \beta H_2O + 3.77\alpha N_2 \Rightarrow$ products
- α is the stoichiometric coeff. varies from 0.0 to 1.0
- β is the stoichiometric coeff. varies from 0.0 to 1.2
- Main process parameters are air ratio, S:C ratio, preheat temperature and reactor pressure.
- H_2 content is much lower due to the dilution of N_2 from the reactant air.

Y. S. Seo, A. shirley, S. T. Kolaczkowski, J. of Power Sources 108(2002) 213-225

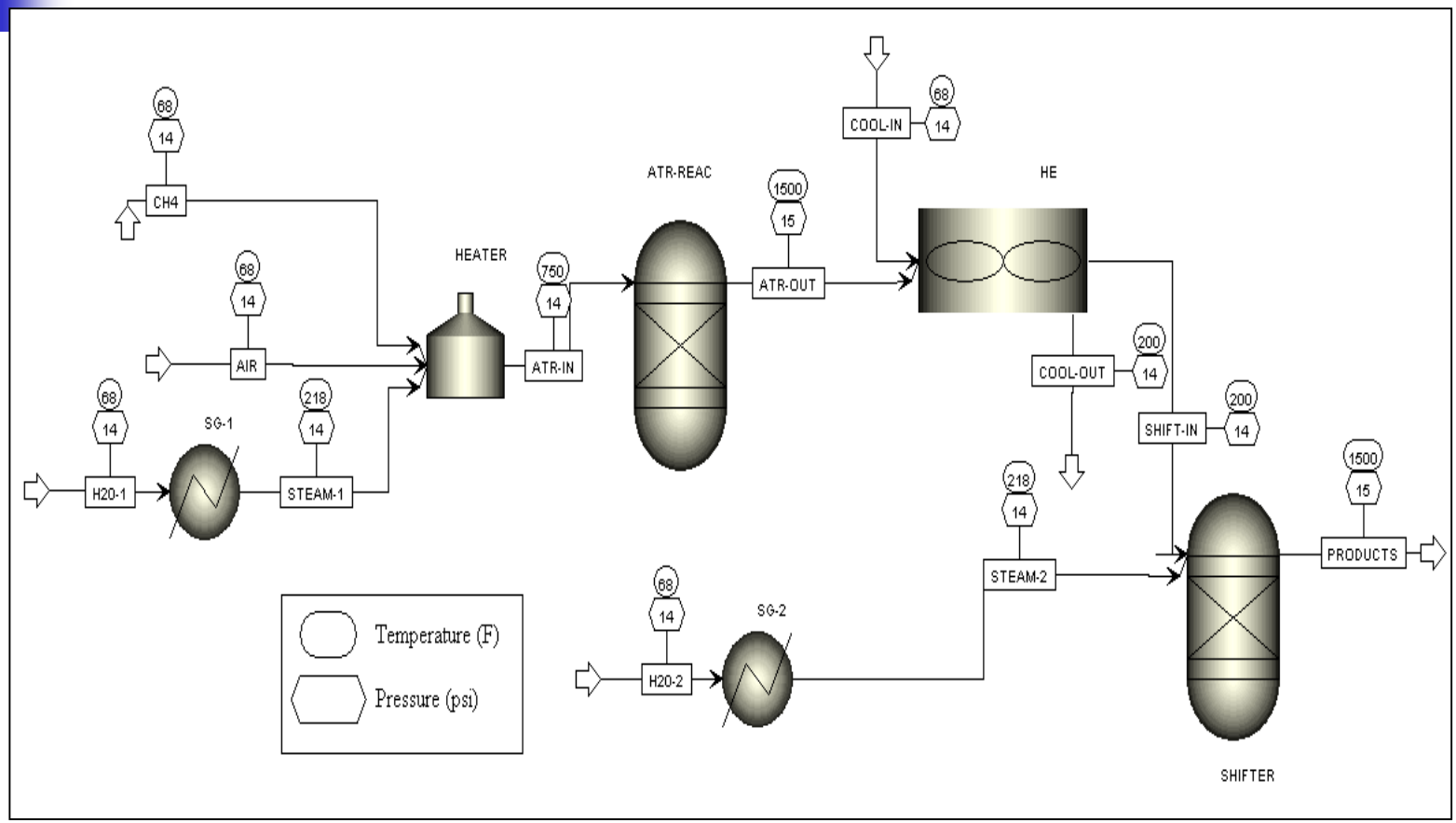
Process Flowsheet- SMR Process



Process Flowsheet- POX Process



Process Flowsheet- ATR Process



Findings and Remarks

- For H_2 generation CH_4 can be reformed by SMR, POX or the ATR processes
- Thermodynamic equilibrium can be reached in all cases
- ATR process is more flexible than SMR for start-up and load change
- SMR reforming system has the highest CH_4 and POX system has the lowest CH_4 consumption.
- POX reforming system is superior to the other systems in terms of the energy cost to produce the same amount of hydrogen from CH_4

Sulfur-Iodine Cycle

- Work is beginning on the inputting of this cycle into ASPEN-PLUS.
- Little progress has been made to this point.

Progress with Cycle Literature Survey

- Found 93 new references. 37 refer to S-I and UT-3.
- Through these references two new cycles have been identified.
- NERI database has been checked. Corrections, ranging from minor to significant, have been made.
- About a dozen cycles have been identified that are not in the database.

Simulation of Reactor Flow

- In this project, hydrogen is generated by decomposing methane at a high temperature (~2000 K) inside the solar thermal reactor.
- The chemical reaction is

  $CH_4 \rightarrow C + 2H_2 \quad \Delta H_{298K} = 75\ kJ/mol$
- Several parameters have been defined, including dimensions and information on the porous medium.
- Materials: inner cylinder-graphite, outer-quartz.

Parameter Calculation

Permeability

$$\alpha = \frac{D_p^2 \in^3}{150(1-\in)^2}$$

where

α - Permeability, m^2

$\in$ - Porosity

D_p – Pore diameter, m

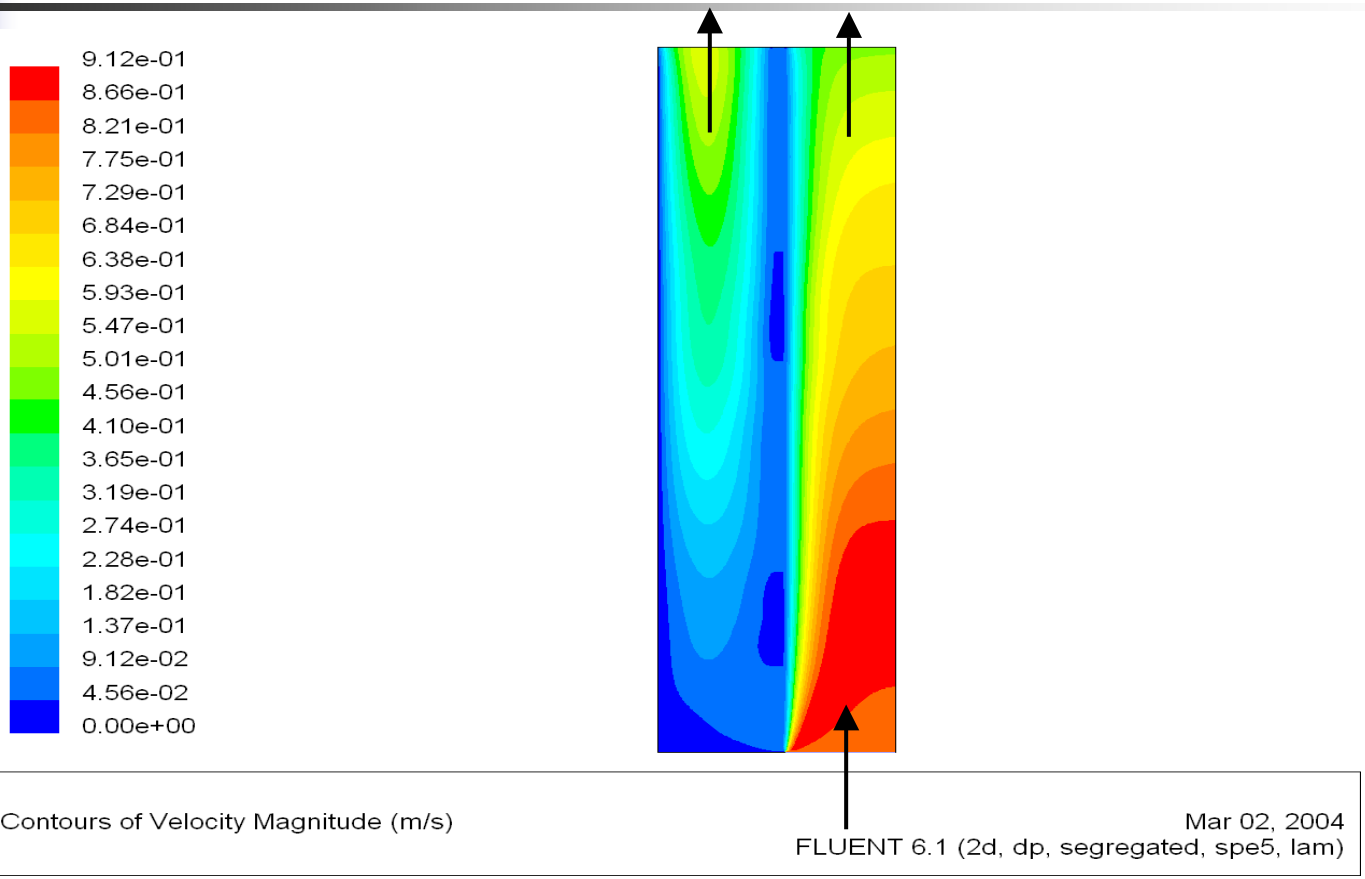
Inertial Resistance Coefficient

$$c_2 = \frac{3.5(1-\in)}{D_p \in^3}$$

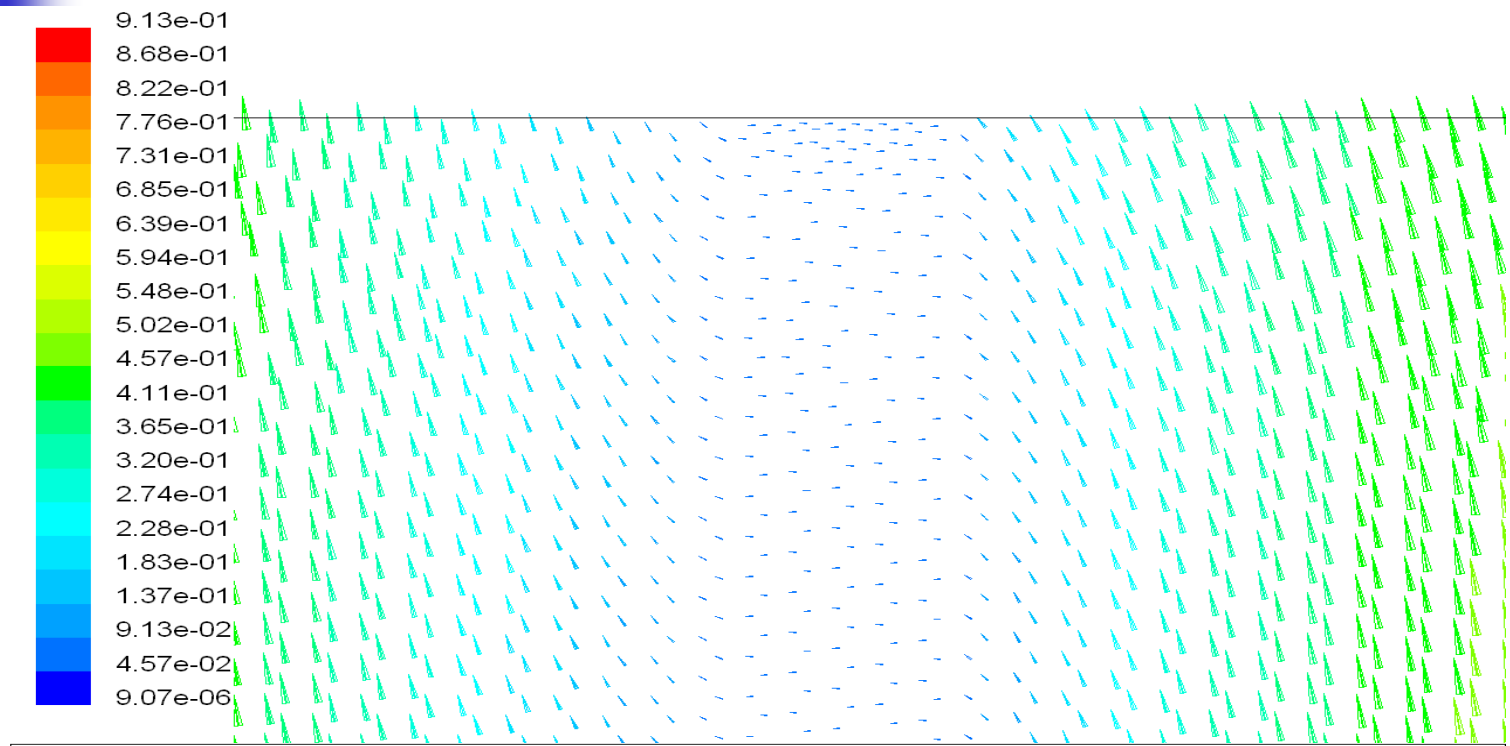
Current Work

- Analyze velocity, temperature, pressure under selected pore diameters.
- Analyze hydrodynamics of the flow.
- Analyze pressure drop after the flow passes through porous medium.

Velocity Contours of Reactor



Velocity Vectors of Reactor



Basic System Design Issues

- Initial design developed will be driven by a dish system unit, irrespective of what is deemed most appropriate for production. One at UNLV can be used.
- Two general approaches are to have a reactor on the unit (less likely) or the reactor ground based near the unit.

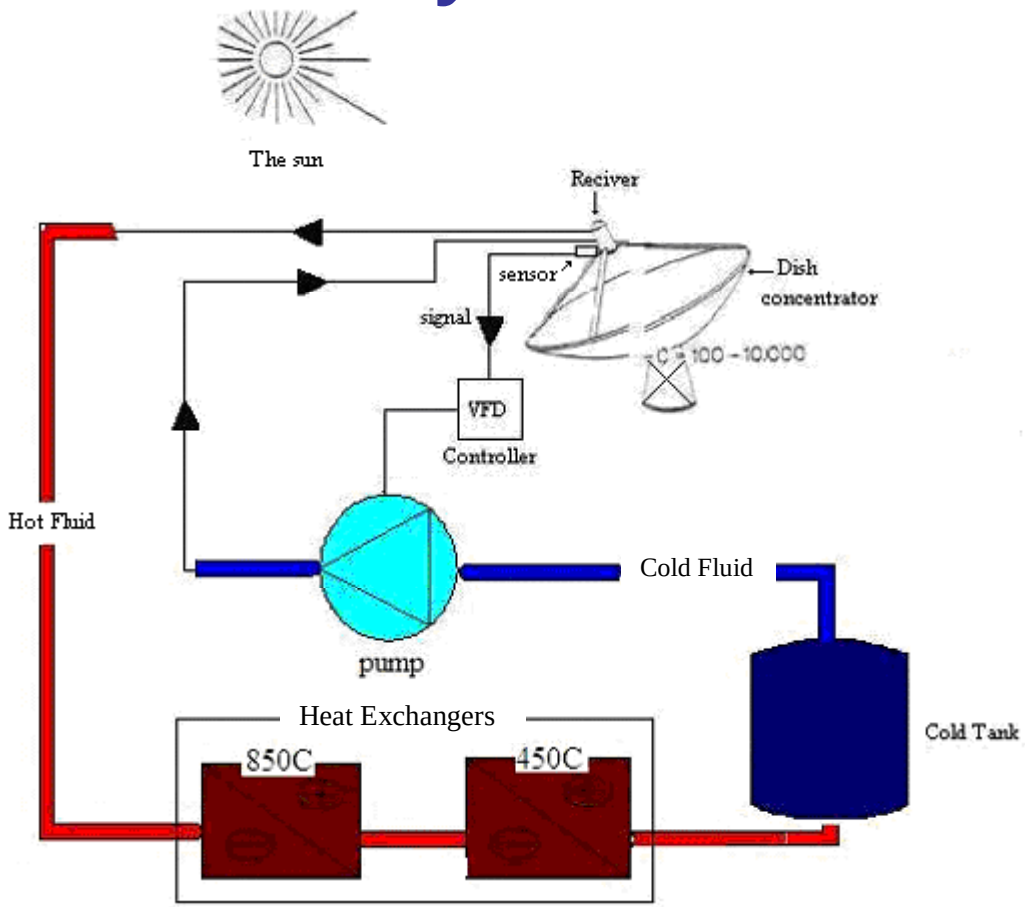
Basic System Design Issues (Cont.)

- Two fluids are being considered: molten salt and air.
- A great deal of experience has been logged with both types of fluids.
- For the initial design, air is currently the most probable candidate.

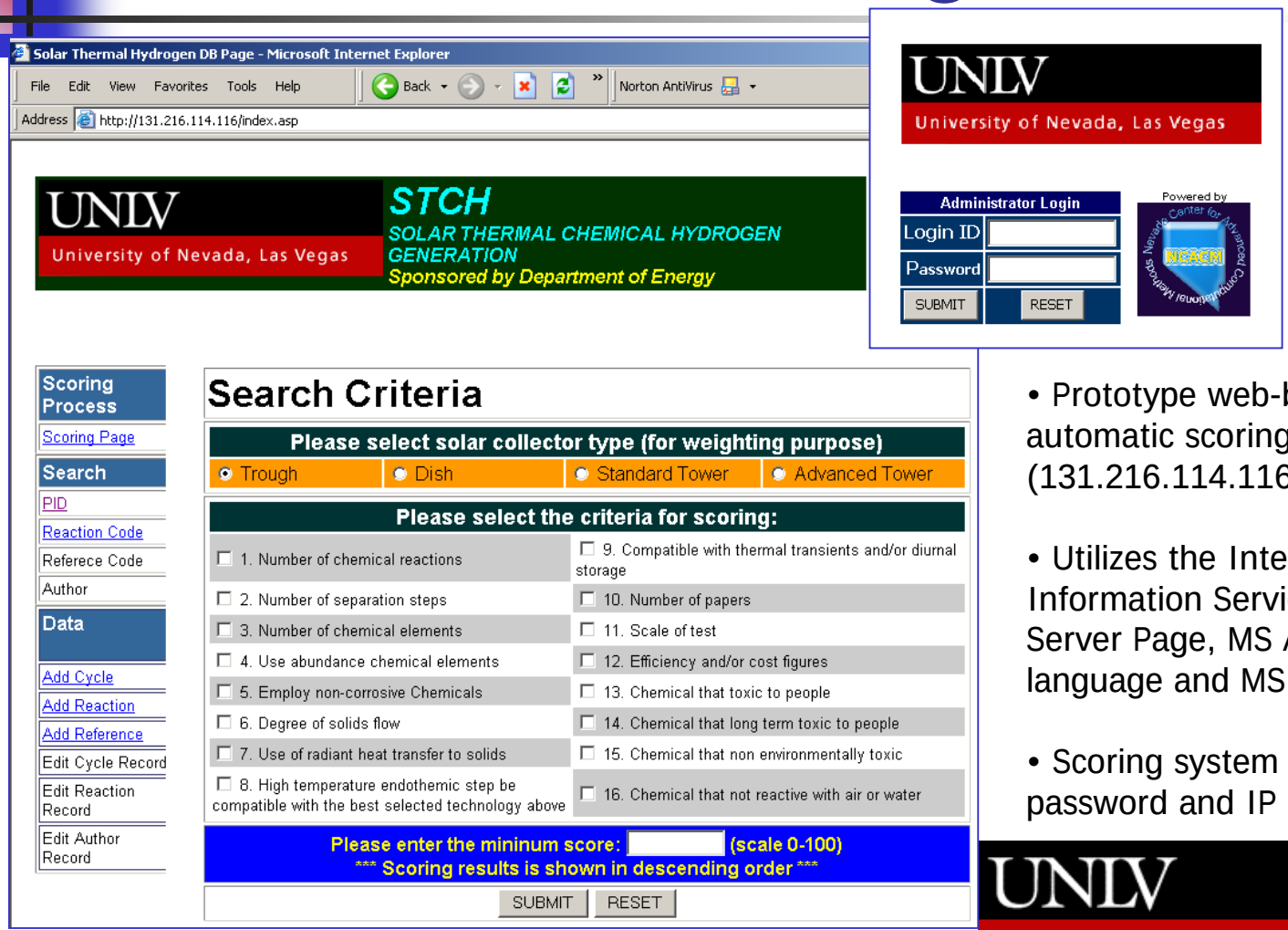
Basic System Design Issues (Cont.)

- A ground-based heat exchanger and reaction chambers will be included.
- Supplemental heat will be available.
- Careful calibration simulations of the unit will allow easy evaluations of design changes and scale-up.

A Possible System



Automatic Scoring Process



- Prototype web-based automatic scoring system (131.216.114.116)
- Utilizes the Internet Information Service, Active Server Page, MS ACCESS, SQL language and MS VB.
- Scoring system is protected by password and IP restriction.

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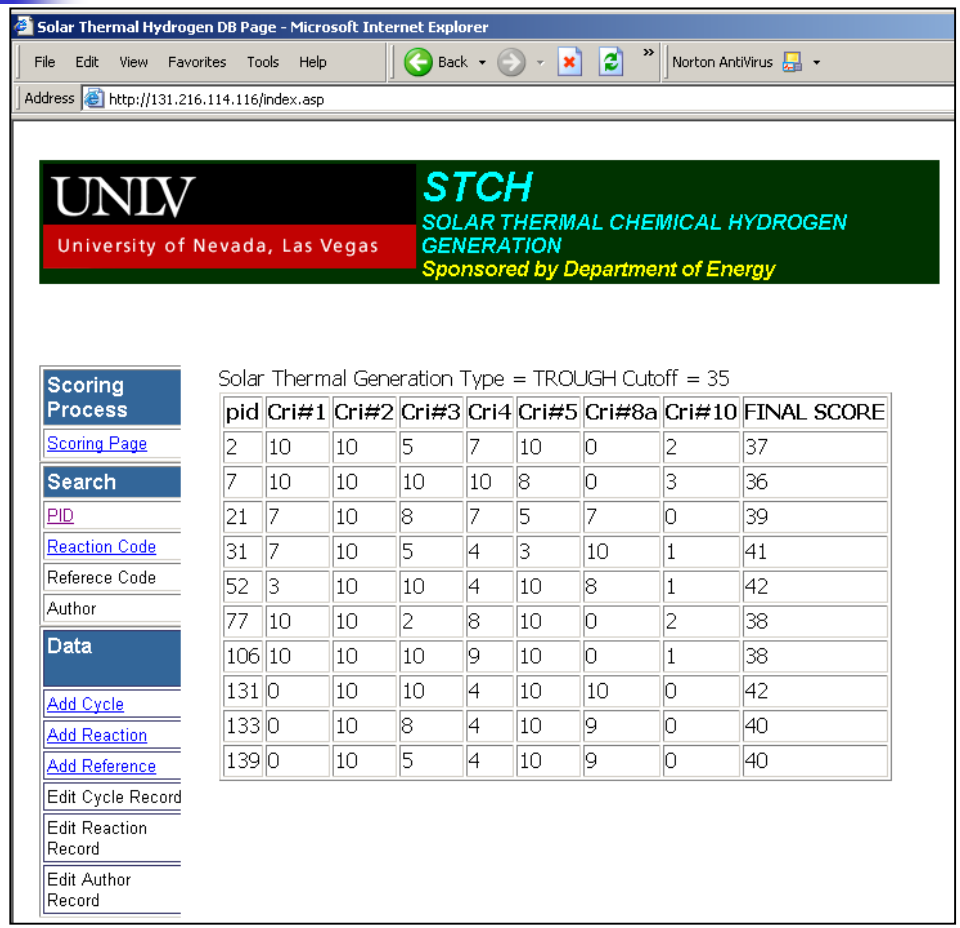
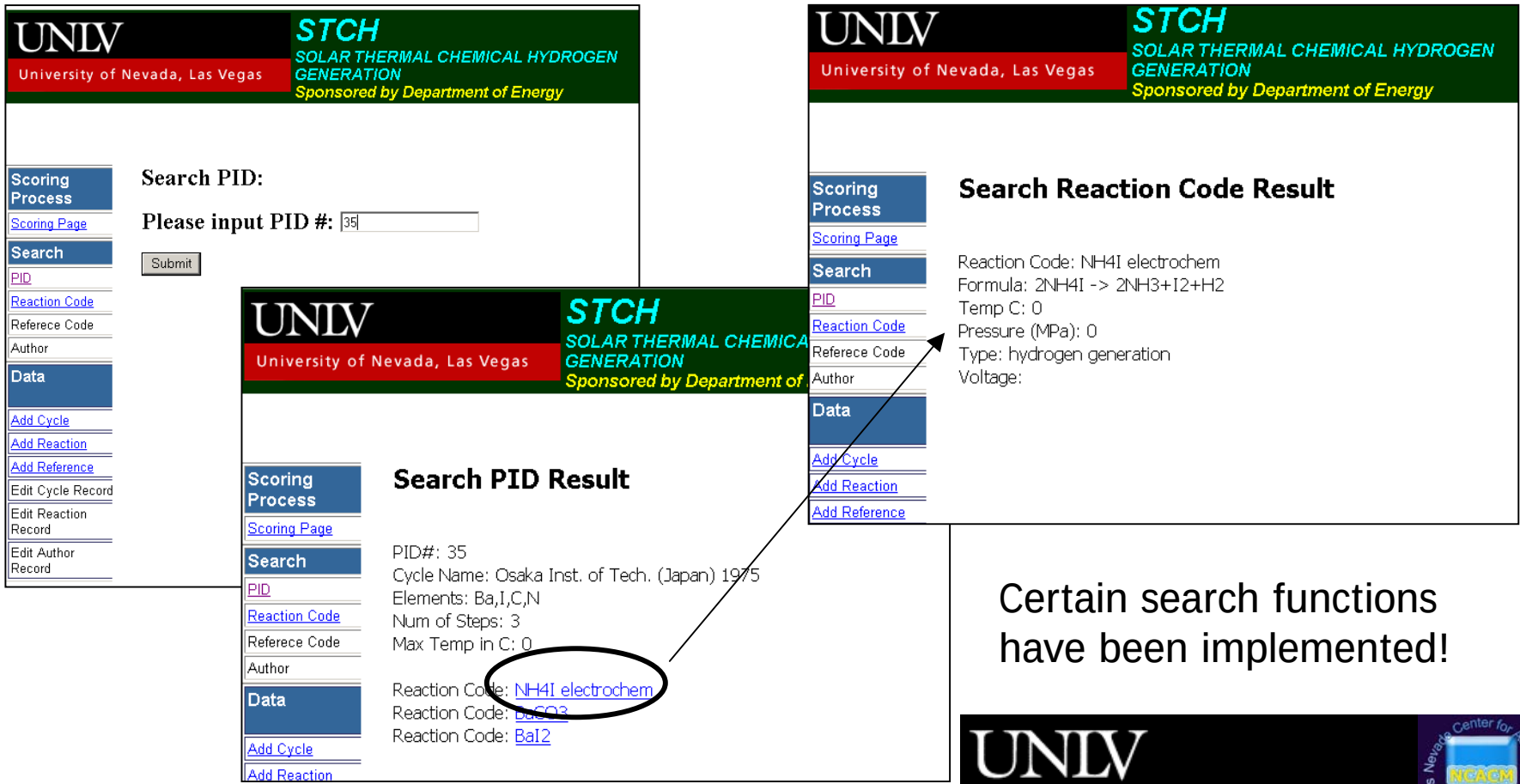
Automatic Scoring Process (contd.)



pid	Cri#1	Cri#2	Cri#3	Cri4	Cri#5	Cri#8a	Cri#10	FINAL SCORE
2	10	10	5	7	10	0	2	37
7	10	10	10	10	8	0	3	36
21	7	10	8	7	5	7	0	39
31	7	10	5	4	3	10	1	41
52	3	10	10	4	10	8	1	42
77	10	10	2	8	10	0	2	38
106	10	10	10	9	10	0	1	38
131	0	10	10	4	10	10	0	42
133	0	10	8	4	10	9	0	40
139	0	10	5	4	10	9	0	40

- The current scoring system takes criteria identified from criteria list, 1,2, 3, 4, 5, 8 and 10.
- Some criteria require manual identification and will be discussed in detail by Sean.

Search Engine
- Cycle (Primary ID) search



Certain search functions have been implemented!

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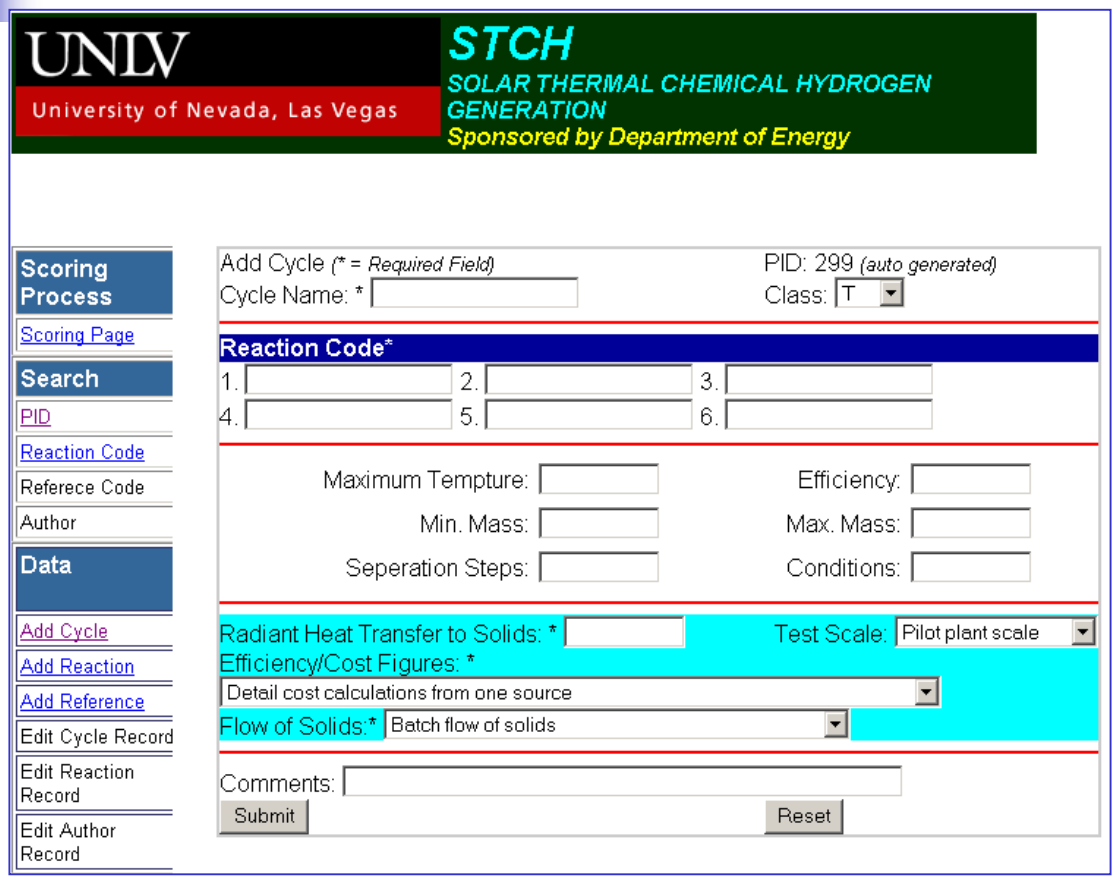
Data Management
- Cycle Update



The interface also serves as a Data Management System that can be used to update the data, create new cycle/reaction simply from any web browser!
(MAC machine ???)